



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 20/18, B65D 65/38	A1	(11) International Publication Number: WO 96/40429 (43) International Publication Date: 19 December 1996 (19.12.96)
(21) International Application Number: PCT/US96/08558 (22) International Filing Date: 4 June 1996 (04.06.96) (30) Priority Data: 08/477,740 7 June 1995 (07.06.95) US PCT/US96/00258 11 January 1996 (11.01.96) WO (34) Countries for which the regional or international application was filed: US et al. (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: VISIOLI, Donna, Lynn; 38 Austin Circle, Lower Gwynedd, PA 19002-2070 (US). (74) Agent: FOWELL, Peter, A.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, CA, JP, KR, NZ, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: SULFIDE SCAVENGING PACKAGING MATERIALS (57) Abstract <p>A packaging material, which is capable of absorbing trace amounts of volatile odorous sulfur compounds particularly from food, is made from a structural support material which is preferably a polymer film, and a defined molecular sieve. The packaging material may be in the form of a film which forms at least one layer of a film package, or it may be in the form of a cap liner, or it may be in the form of an insert. Film materials may be oriented film or oriented shrink film. The molecular sieve may be defined either by its measured ability to adsorb hydrogen sulfide, or by certain physical and chemical structural parameters of the molecular sieve. These are pore-opening size, Si/Al atomic ratio, pore-structure dimensionality, and basicity.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

SULFIDE SCAVENGING PACKAGING MATERIALS

Cross Reference to Related Application

This application is a continuation-in-part of copending
5 Application, Serial No. 08/373,825, filed January 17, 1995.

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates generally to packaging materials
which enhance freshness by removing hydrogen sulfide and other odorous sulfur
10 products from certain foods and non-food protein sources. More specifically,
the packaging materials of the present invention comprise a defined molecular
sieve enclosed by a polymer film or sheet, or embedded within a polymer film
or sheet, particularly when the film or sheet is oriented, and even more
particularly when it is also heat-shrinkable. The packaging materials may be
15 used as a packaging structure (i.e., a package itself such as a film package), a
layer of a film package, or a package insert such as a coupon or liner.

Description of Related Art

In food packaging, the principle emphasis in relation to odor
removal has been with the packaging material itself. Many polymeric
20 packaging materials produce odors which can impart an undesirable odor to the
food. Various additives have therefore been added to the polymer to remove its
odor. However food itself, even while it remains in good condition, can
produce undesirable odors, and some of the odor producing substances have
such a low odor threshold that trace amounts are undesirable. In addition, trace
25 amounts of such substances can produce an off-taste in food.

Sulfur compounds having undesirable odor can originate from
proteins and free amino acids in foodstuffs. They may originate from sulfur-
containing amino acids of fresh, cooked or preserved foods including meats
particularly poultry, cheese, dairy products, eggs and ovalbumin. Among these
30 are sulfur-containing compounds, including hydrogen sulfide, mercaptans,
sulfides and disulfides. These sulfur compounds can discolor cans containing
such food, and there has been an abundance of work directed to can coatings to
prevent this discoloration. However, a more important aspect is the presence of
the odor, and often an associated taste, in the food itself. The odor threshold of
35 some of these is very low (10 micrograms/liter or less) so that even small

amounts can, as noted, be very objectionable well before any real deterioration of the food has occurred.

Packaging materials are commonly polymeric films. These may be essentially unoriented, or oriented in either one or two directions. Oriented
5 films may also be heat shrinkable. Orientation of films may be used merely to improved mechanical properties. There is a vast patent literature of preparation of oriented films. Orientation is carried out in controlled temperature ranges typically well below melt processing temperatures, and commonly near the
10 melting point or glass transition temperature, where molecular orientation occurs and the film does not tear. The temperatures allow sufficient mobility to orient, yet sufficient lack of fluidity to hold the orientation until the film is cooled or quenched. Oriented films may be annealed to reduce or remove any heat-shrinkable nature, or they may be oriented and subsequently treated in such a way as to provide and maintain a heat-shrinkable nature. Typically, the film is
15 cooled in the stretched state and upon subsequent heating, the film shrinks in seeking to recover to its original dimensional state.

U.S. Patent No. 3,141,912 describes a process for making heat shrinkable film that has achieved considerable commercial utility. Here the polymer is extruded into a film tube which is then quenched to a temperature
20 below the orientation temperature range, and is reheated to the orientation temperature range, followed by biaxially stretching of the film of the tube while within this temperature range. The biaxial stretch is done by (a) using internal gas pressure to expand the diameter of the tube to form a large 'bubble' and (b) advancing the expanded tube at a faster rate than the extrusion rate so as to
25 obtain transverse and machine direction orientation. The patent is hereby incorporated by reference.

U.S. Patent No. 4,820,557 discloses the manufacture of multilayer heat shrinkable film in which one of the layers is a linear copolymer of ethylene with either 1-octene or 1-hexene.

30 U.S. Patent No. 4,597,920 discloses the manufacture of heat shrinkable film by the process of U.S. Patent 3,141,912 wherein the linear copolymer is of ethylene with at least one C8-C18 alpha-olefin. The commercial shrink film of ethylene/1-octene of this process is called Clysar® LLP shrink film. The patent, 4,597,920 is hereby incorporated by reference.

35

Oriented, and particularly heat-shrinkable film can be particularly adaptable to packaging, including food packaging. Continuous packaging machines which pack chicken parts in a tray, for instance, may advantageously employ shrink film.

5 Many materials can remove sulfides by reaction with them. Metal oxides, particularly zinc oxide have been used. Industrially, removal of sulfides in various processes is often carried out by reaction. In general, using chemical reactions to remove sulfides is fine in chemical processes, but not very
10 controllable for food use, both because of toxicity concerns and the difficulty of controlling any such process. Adsorption is an alternative to reaction. Many adsorbents are unsuitable for contact with food. However, while several adsorbents may be entirely suitable for contact with food, there appears to be no work directed specifically to removing trace amounts of sulfur-compound related odors from food with their use.

15 Packaging materials capable of scavenging specific decomposition products from food have been disclosed in U.S. Patent No. 5,284,892 (Brodie and Visioli). Specifically, aldehydes are scavenged by a polyalkylene imine of greater than 800 molecular weight. The imine is incorporated into a packaging film or sheet. Similar scavengers are disclosed in
20 allowed Patent Application, serial number 08/176,740, which extends their use to packaging structures which include liners, inserts and the like. Polyalkylene imines are unsuitable for direct food contact, and so when used, the required packaging structure has to ensure that the imine does not contact the food.

Molecular sieves are materials of varying composition which
25 have a three dimensional cage like structure which form channels with defined mouth opening (aperture or pore-opening) sizes. They may be naturally occurring materials, modified natural materials, or essentially synthetic. They include silicas, metalloaluminates, aluminophosphates and various others. The silicas may be subdivided into titanosilicates, aluminosilicates, gallosilicates, ferrisilicates, borosilicates, chromosilicates and others. Among the
30 aluminosilicates are the zeolites. Specific zeolites have been used for different purposes including catalysis, sieving and adsorption. Typically, zeolites are defined by parameters such as Si/Al ratio, their pore-opening size and structure, acidity, the cations present and others.

Clays may also be aluminosilicates also containing magnesium, but typically have a laminar structure, not a three dimensional structure.

Japanese published application, J61,120,638A discloses an adsorbent composite for packaging consisting of a polyolefin related resin and an adsorbent. The adsorbent is broadly disclosed to be any of a diverse range of materials including silica gel, activated alumina, acid clay, activated clay, zeolites or active carbon. Uses include dehumidifying and deodorizing pharmaceuticals, foods, or precision machines.

U.S. Patent No. 4,795,482 (Gioffre et al.) discloses a process for removing odors from an 'environment', using certain specific hydrophobic, high silica zeolites and so-called silica polymorphs. Odors removable include those caused by a vast range of volatile materials including certain acids, aldehydes, organic nitrogen contain compounds and sulfur compounds including mercaptans and sulfides. Applications include powders, sprays, pads, creams, mouthwash, and non-woven tissues for treatment of odors in bathrooms, kitchens, refrigerators etc.

U.S. Patent No. 5,011,019 (Sato et al.) discloses a packaging structure for packaging medicines which may emit foul odors caused by substances such as carbonic acid, trimethylacetic acid and hydrogen sulfide. The package enclosing the medicine has a metal press-through side, and a multilayer polymer side, one layer of which is an polyolefin layer which incorporates deodorizing materials. The deodorizing materials mentioned as suitable include inorganic metal salts, favonoid, and unspecified molecular sieves.

There remains a need in the art for a packaging material, particularly in the form of oriented film which may also be heat-shrinkable, which can be used safely in contact with food, used either as a package itself, or as a packaging insert, specifically designed to remove hydrogen sulfide, mercaptans, sulfides and other odorous sulfur compounds from the specific foods which generate this odor, thus increasing shelf life.

SUMMARY OF THE INVENTION

The present invention is directed to novel packaging materials which form packaging structures or package inserts capable of adsorbing sulfur-compound odors generated by certain foods. The packaging material comprises a particulate aluminosilicate or silica molecular sieve, and an associated

structural supporting component in the form of oriented film, and especially heat-shrinkable film.

In the broadest aspect of the invention, the molecular sieve suitable in the packaging material may be functionally defined as any
5 aluminosilicate or silica having a zeolite-type structure where 5 mg. of it is capable of adsorbing at least 25% of hydrogen sulfide present in a GC vial of volume 22.5 ml. at a concentration of 12,000 ppm, in 15 minutes at a temperature of 25 +/- 2 deg. C.

Alternatively, the molecular sieve may be structurally defined as
10 an aluminosilicate or silica having a zeolite-like structure which has a three dimensionally-connected pore-structure all of whose pores-openings have a minimum diameter of about 4 Angstroms, a Si/Al atomic ratio of 1 or greater, and has substantially all of any associated cations those of the metals of group 1A and group 2A metals.

15 The associated structural supporting component may be in the form of a film or sheet, particularly oriented film, either enclosing the molecular sieve or acting as a matrix having the molecular sieve embedded in it. The oriented film may further be heat-shrinkable. The supporting component must be permeable to sulfides and mercaptans. When the molecular sieve is
20 embedded in the supporting component it is present at a level of from 0.1 to 10 weight percent, preferably from 0.5 to 5 weight percent.

The packaging materials comprising the molecular sieve and the associated supporting component may be formed into a package structure itself, the packaging material forming the package walls or part of the package walls,
25 such as a layer in a laminate. Or it may be in the form of an insert such as a coupon, a cap liner and the like.

DETAILED DESCRIPTION OF THE INVENTION

In literature on molecular sieves the words or phrases 'channel', 'pore' 'pore-structure' 'aperture', 'pore-opening size' and 'pore-size' tend to be
30 used loosely, some with considerable interchangeability. In this disclosure we describe the materials as having 'channels' which form an overall 'pore-structure'. The openings through which molecules can penetrate we will refer to as 'pore-openings' having a 'pore-opening size'. They will be described as 'powders' consisting of 'particles'.

Molecular sieves can reasonably be said to either absorb or adsorb gases to describe the same gas take up. In this disclosure the words adsorb and adsorption are preferred.

While there are a large number of materials which can react with sulfides, mercaptans and other sulfur compounds, as well as a large number of adsorbents of various types which can absorb various gases, surprisingly, in an investigation of many materials and adsorbents tried as sulfide odor removers, only a few defined molecular sieves have been found which are suitable to form part of the packaging materials of this invention. Even among molecular sieves, many are quite unsuitable, and only those with very specific characteristics are useful.

First and foremost, the molecular sieves of this invention are aluminosilicates or silicas having a zeolite-type structure. Many other metallosilicates are known, but the aluminosilicates and silicas have the major advantage of being, in general, non-toxic, and suitable for use where contact with food can or does occur. Furthermore, when blended with many polymer films, the film remains transparent, which is a major advantage in packaging films. This is because, the particle size is sufficiently small - typically, from about 0.1 to 10 microns. The lack of toxicity contrasts with packaging materials described in U.S. Patent 5,284,892, where the structure of the packaging material must prevent contact of a polyalkylene imine with food, due to its lack of acceptability in this regard. In the present invention, while it is preferred not to have small amounts of the adsorbent mixing with the food, with these materials there is no toxicity problem should they do so. Indeed, many such materials are actually used in food. Thus certain zeolites are used as moisture adsorbers admixed with table salt to allow it to pour freely.

While the primary use of the materials invention of this invention is for food packaging, use to package other products which emit sulfur-related odors, such as preparations to alter structure of non-food proteins, such as home permanent wave preparations is also contemplated.

The suitable molecular sieves of this invention are aluminosilicates or silicas having a zeolite-type structure, which are capable of absorbing a specific amount of hydrogen sulfide from an atmosphere containing it. Specifically, they are those where 5 mg. of it is capable of adsorbing at least 25% of hydrogen sulfide present in a GC vial of volume 22.5 ml. at a

concentration of 12,000 ppm, in 15 minutes at a temperature of 25 +/- 2 deg. C. It is within the skill of the artisan to determine readily whether any particular molecular sieve is suitable by this simple test.

Alternatively, the suitable molecular sieve may be defined in structural terms. The critical structural parameters suitable for selecting the aluminosilicate and silica molecular sieves for the purposes of this invention are known for many such materials, but those parameters have not been determined for many others. Thus it may be immediately possible to say a given aluminosilicate or silica is suitable for use in the present invention if those parameters are known. In cases where those parameters are not known, the functional testing described above will determine suitability.

In order to describe these critical structural parameters which determined suitability, it is first necessary to describe the structure of the particular molecular sieves which are useful in the invention.

The molecular sieves which form part of the packaging materials of this invention are complex aluminosilicates or silicates characterized by a three-dimensional framework structure, enclosing cavities and channels. (These are often also referred to loosely as pores; the ends of the channels are usually described as pore-openings, or apertures, and the system of channels is said to have a pore structure). The channels may be occupied by ions and water molecules, all of which can move with significant freedom within the zeolite matrix. The water molecules can be removed or replaced without destroying the essential geometry. They may be naturally occurring, modified naturally occurring materials, or synthesized. They can be represented by the formula:

$$(M_2/nO) \cdot (SiO_2)_x \cdot (Al_2O_3)_y \cdot (H_2O)_y$$

though the aluminum may approach zero, in which case the material will be referred to as a crystalline silica (not silicate). M is a cation of valence n, where the cation may be metallic or a proton. In those naturally occurring molecular sieves commonly known as 'zeolites', x is generally from about 2 to 8. And y may be 1 or more. There also exist synthesized, so-called high silica zeolites, and more generally aluminosilicate molecular sieves with extremely high levels of silica to alumina, approaching infinity; that is to say only trace amounts of aluminum are present. In that case, the material is, as noted above, essentially a silica. The cation is associated, primarily, only with the alumina, so that the less aluminum present the fewer cations. For the purposes of this invention, the

term molecular sieve will be used, because the term zeolite is often defined as a material having a specific amount of aluminum, and at very low aluminum levels, approaching trace amounts, most common usage of the term zeolite would exclude such materials.

5 In naturally occurring zeolites, M is Na, Ca, K, Mg and Ba in varying proportions. The cations can be changed by ion exchange, and other ions such as Cs or Sr can be introduced. The structure consists of corner-linked tetrahedra with Al or Si atoms at the centers and oxygen at the corners. The tetrahedra are combined into repeat structures of 4 to 12 membered rings
10 resulting in a framework with regular channels and 'cages' at channel intersections. The channels may be one dimensional (i.e., tubular) with the tubes not connected, two dimensional where channels branch to other channels, but each series of two dimensional channels is not connected, or a three dimensionally-connected system of channels. Here molecules which are
15 sufficiently small can travel freely throughout the channel system or pore-structure. In some cases there are two separate interpenetrating (but not connected) three dimensionally-connected systems. The channels and cages impart a pore-structure with differing dimensions which are critical to movements of molecules into and within the channels and cages, the pore-
20 openings controlling access to the interior of the zeolite. The pore-opening dimensions are determined not only by the tetrahedra forming the pore-opening, but by the ions in or near the pore-opening. In many cases the pore-opening is aspherical or generally asymmetrical, and can have a smallest and a largest diameter. The smallest diameter will clearly control access of molecules.
25 Overall, the variations within the zeolite structure create a wide variation in utility for various zeolites. The same situation is true for molecular sieves even when the amount of aluminum approaches just trace amounts.

 The molecular sieves suitable for this invention, have a Si/Al atomic ratio which can range from 1 to infinity. By infinity is meant none or
30 only trace amounts of aluminum are present. The ratio may be determined by standard wet chemical methods or by atomic adsorption spectroscopy. In describing this type of material, it is common to use the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ rather than Si/Al, since this characterizes the chemical units which make up the structure. However in this disclosure, the Si/Al atomic ratio is used. It is of
35 course readily possible to calculate one from the other.

The molecular sieves of this invention also have a three dimensional pore-structure, and a minimum pore-opening size of about 4 Angstrom. Pore-opening size may be somewhat temperature dependent, and since adsorption in end use has to take place at ambient temperatures, the pore-opening size refers to the size which will be present at ambient temperatures, that is to say between about 20 and 30 degrees C. Methods of determining and calculating pore-opening size are well known in the art, and many molecular sieves have established pore-opening sizes.

Useful references generally relating to zeolite-type structure and characterization include the following: Meier et al., 'Atlas of Zeolite Structure Types' (International Zeolite Assn. 1978); Mumpton, 'Natural Zeolites' in Reviews in Mineralogy 14:1 (1977), and Smith, 'Origin and Structure of Zeolites' in Zeolite Chemistry and Catalysis, ACS Monograph 171, American Chemical Society, 1976.

If the pore-opening is asymmetrical, the 4 Angstrom minimum refers to the smallest diameter. In addition, the molecular sieve must be basic, in that substantially all (i.e. more than about 90%) the associated cations can not be hydrogen ions, but must be a metal ion of group 1A or 2A, preferably Na, Ca, Ba, Mg and K, preferably Na and Ca. Ion-exchange with other metals such as zinc (group 2B) are also possible. As the amount of aluminum approaches zero, the number of associated cations approaches zero, and the material will become increasingly neutral. Molecular sieves falling within these limitations are suitable.

The molecular sieve's pore-opening size will be large enough to let through the smallest odor causing sulfur compound molecules. The pore-opening size of molecular sieves is a fairly precisely definable quantity. The diameter of molecular species which are to be adsorbed however is more difficult to define. Various types of measurement have been used to determine diameter, and various methods of calculating different aspects of the size of the molecule have been used. When a molecule is unsymmetrical, as in longer chain mercaptans, it becomes difficult to know what dimension of the molecule is important in relation to its ability to enter a molecular sieve having defined minimum pore-opening size. There is a crude correlation between pore-opening size and molecular size. Hydrogen sulfide has a Lennard-Jones 'kinetic' diameter of 3.6 Angstroms and a Pauling length by width of 4.6 X 3.9

Angstroms. These numbers are in line with what has been found to be the minimum pore-opening size allowable for adsorption of hydrogen sulfide, namely a pore-opening size of about 4 Angstroms.

Hydrogen sulfide is the principle odor causing compound from
5 foods which generate sulfur compounds. Other sulfur containing odor causing compounds of importance are slightly larger in size, but some have a much lower odor threshold than hydrogen sulfide. If we use a value of 4.23 Angstroms for the diameter of hydrogen sulfide, one calculation/measurement/estimate of the size of various odor-causing materials
10 made by the inventors suggested the following sizes (in Angstroms): methylmercaptan 4.80; ethylmercaptan 5.22; dimethyltrisulfide 5.43; dimethylsulfide 5.63; and methional [3-(methylthio)propionaldehyde] 6.17. The odor threshold however is in quite a different order. Thus values quoted in 'Food Chemistry' by H.D. Belitz et al. 1987, gives the following values in
15 micrograms per liter: hydrogen sulfide 5; methylmercaptan 0.02; ethylmercaptan 0.008; dimethyltrisulfide 0.01; dimethylsulfide 1.0; and methional 0.2. While, as will be described below, sieves with a minimum pore-opening of about 4.0 Angstroms adsorb hydrogen sulfide provided the other structural parameters are met, for adsorption of other odor-causing sulfur compounds, it is preferred to
20 have a pore-opening size of greater than about 5.5 Angstroms.

There is no particular particle size limitation for the molecular sieve. However, for adequate surface area for rapid adsorption, it is preferred that the particles be from 0.1 to 5 microns. When molecular sieve particles are incorporated into a film layer of a package (i.e., as a filler), the particles should
25 preferably have an average diameter less than half the film thickness, and a size distribution such that no particles have a diameter as thick as the film, and preferably less than three quarters of the thickness of the film. This represents no real problem, since a 1 mil. (25 micron) film could have particles, by this criterion, of 12 microns in diameter which is higher than typical sieve particles.
30 The adsorbent layer may be from about 1 to 5 mils.

The particulate molecular sieve adsorbent obviously is not mixed directly with the food, and is kept separate from it. The adsorbent is part of a packaging material, the packaging material comprising the adsorbent and an associated structural supporting component. By this, is simply meant another
35 material which contains (i.e. as a filler), encloses, or otherwise supports the

particulate adsorbent so that the individual adsorbent particles can not readily separate from the packaging structure and mix with the food. Thus, the adsorbent may be melt blended, just as with any particulate filler, into a polymer which is then made into a film which forms the walls of a package container, herein referred to as a 'film package', or part of the walls of a packaging container. The package may be a film pouch. The pouch of course may be further enclosed in some other packaging material such as a cardboard carton.

The packaging material of the invention when it is in the form of an adsorbent-filled film may be one layer of a multilayered film or sheet, with other co-extruded or laminated and adhered layers acting as water or oxygen barriers etc. If there are other layers, the adsorbent-filled layer may be the layer which contacts the food, unlike the situation where the adsorbent is not suitable for food contact such as polyethylene imine aldehyde scavengers. It may however be another layer, provided any inner layers (those between the adsorbent layer and the food) are permeable to the odor-causing sulfur compounds, so that they may pass through it to contact the adsorbent-filled layer. For instance the inner layer could not be a metallic film layer or highly crystalline polymer or poly(vinylidene) chloride which is a useful barrier. If there is an inner layer, it should not be more than 3 mils thick.

The invention can advantageously employ various sorts of oriented and shrink film. Typical shrink films which may be used in this invention are Clysar® shrink films, which are various polyolefin copolymer films manufactured by E. I. du Pont de Nemours and company. They include mono- and multilayer films of polyethylene and polypropylene. The invention will be suitable for many other shrink films however. Incorporation of particles of such materials as silica into films, including shrink films, is routinely carried out, and is well known in the art. Incorporation of the adsorbents of this invention will present no unusual difficulties, provided the limitations on particle size, as noted above, are met. The adsorbent may be incorporated into the film directly, during film extrusion, or made into a polymer concentrate to blend during the film extrusion process, before the orientation process.

Alternatively, the package material may not be part of the package itself, but may be a free insert, such as a coupon. Or it may be an insert which does form part of the package, such as a cap liner. When the packaging

material is a free insert, a possibility within the bounds of the present invention is that of the particulate adsorbent enclosed, i.e. encapsulated by a polymer film or other material, but not blended (i.e., as a filler) within it. Other materials which could be used to encapsulate molecular sieve particles are non-woven materials. These would act as ideal encapsulating materials since they are highly porous, provided the pores of the non-woven are not of a size which would let through the molecular sieve particles.

Polymers suitable as the associated structural supporting component are olefinic homopolymers such as polypropylene, polyethylenes such as LDPE, LLDPE and ULDPE, copolymers of ethylene and vinyl esters such as vinyl acetate, and copolymers of ethylene and unsaturated acid or esters of those acids such as acrylic or methacrylic acid, or 1-8 carbon alkyl acrylates and methacrylates, or mixtures of these comonomers. Also included are ionomers of ethylene/acrylic acid or methacrylic acid copolymers and terpolymers. Ionomers are the well known metal ion partially neutralized ethylene/(meth)acrylic acid copolymers, described in U.S. 3,264,272 (Rees) which is hereby incorporated by reference. The polymers preferred as the structural supporting component are polyolefines and polyolefin copolymers (i.e. with other alpha olefins).

In multilayer films used to form packages, one layer of which is the packaging material of the present invention, other layers may be an inner seal layer and outer barrier layers or merely outer bulk layers. Such multilayer films are well known in the packaging industry and there are endless variations of such films. The adsorbent layer is preferably separated from the food to be packaged only by one layer, that layer being a seal layer which contacts the food. Seal layers may be any of the polymers listed above as the structural supporting component, but preferably ionomers or ethylene vinyl acetate which are ideal adhesives. Other layers may be an oxygen barrier layer such as ethylene/vinyl alcohol copolymers, or a moisture barrier layer which may also be the bulk layer. Suitable polymers for this include polypropylene, polyethylene and polyethylene copolymers. The layers may have various adhesives tying them together, such as 'BYNEL' which is the name for certain modified polyolefins manufactured by E.I. du Pont de Nemours and company.

Test Methods

Different potential reactants or adsorbents were evaluated as hydrogen sulfide removers using GC. Either the reactant/adsorbent itself, or the reactant/ adsorbent melt blended with a polymer at a level of 2 parts per 100 parts polymer were placed in a GC vial. Weight of the sample to be tested was 5 mg. when straight powdered adsorbent was tested, and about 8 square inches (4 X 2 inches) of film when film was tested.

Then enough hydrogen sulfide to provide 12000 ppm in the (air containing) vial (based on the volume of the vial which was about 21.5 ml.) or about 250 uL of pure hydrogen sulfide was injected into the vial. After fifteen minutes, the concentration of hydrogen sulfide remaining in the vial was measured. The concentration change was measured by taking out 250 uL of the mixed air/hydrogen sulfide from the vial, and measuring the hydrogen sulfide concentration using standard GC methods. The adsorption was calibrated against a similarly filled vial without adsorbent, to allow for adsorption by the vial septum and vial surface.

EXAMPLES

The invention is illustrated by the following examples.

In the following examples, in Series 1, samples of the potential absorbent were melt blended with 'ALATHON' 1540, a LDPE, manufactured by the Du Pont Co. at a 2 weight percent level, placed in a vial and evaluated as indicated above. A list of the potential adsorbents/reactants tried is shown in Table 1. Results are shown in Table 2. In Series 2, potential reactant/adsorbent was placed directly in the vial and evaluated as indicated above. Results are shown in Table 3. Some potential reactant/adsorbents were tested both in series 1 and 2. In other cases, if a reactant/adsorbent showed no potential in one or the other of the two series, (whichever was tried first with the material) it was not repeated in the other series.

Zeolite M5 (also known as Mordenite) has the required pore-opening sized, but has a one dimensional pore structure. That is to say it has unconnected single channels. Chabazite has a three dimensionally-connected pore structure, but the pore-openings in one of the three dimensions is less than 4 Angstroms. DAY-55 has the necessary pore size, the channels are connected into a three dimensionally-connected pore-structure, but it is acidic, having protons replacing metal ions. Such acidic materials also have the disadvantage

of possible reaction with some of the polymeric packaging components of the packaging material. Zeolites 4A and 5A adsorbed some hydrogen sulfide alone, but not when incorporated into film. The minimum pore-opening is defined as about 4 Angstroms. In any particular sieve the actual minimum may be from
5 3.7 to 4.3 Angstroms. It is surmised that the effective diameter for these zeolites under test conditions may than that quoted, at least in one direction. The zeolites with much larger pore-opening size, Y52 and 13X are clearly better and preferred.

Clays have a laminar structure, not a Zeolite-type three
10 dimensional structure. The various clays tried generally do not perform well in films. They do typically contain a complex of Al_2O_3 and/or SiO_2 and/or MgO , but the structure is inadequate. Bentonite does perform well when tested neat, but not in films. This may be related to interplanar spacing, between
15 'molecules', that spacing disappearing when blended with films. By contrast, the 3 dimensional structure of the zeolite-like structures remain essentially intact when blended with polymers.

TABLE 1

ABSORBENTS/REACTANTS EXAMINED

<u>SUBSTANCE</u>	<u>TYPE</u>	<u>DIMENSIONALITY</u>	<u>PORE Diameter</u>	<u>Si/Al</u>	
<u>ION</u>					
5	Activated alumina	NA	NA	NA	NA
	ZnO/TiO ₂ (1)	NA	NA	NA	NA
	ZnO?Zn phosphate (1)	NA	NA	NA	NA
	ZnO/Al salt/Ni salt (1)	NA	NA	NA	NA
	Mg Aluminate	NA	NA	NA	NA
10	Activated Carbon	NA	NA	NA	NA
	VEEGUM A132A	NA	NA	NA	NA
	VAN GEL B	NA	NA	NA	NA
	Bentonite NF	A Clay	NA	NA	NA
	Bentonite MPS	A Clay	NA	NA	NA
15	Magnebrite HS	A Clay	NA	NA	NA
	Hectabrite DF	A Clay	NA	NA	NA
	Laponite RD	A Clay	NA	NA	NA
	Chabazite (CHA type Zeolite)	3	3.8 x 3.8	2	Ca
20	ABSCENTS 3000 (MFI Sieve)	3	5.3 x 5.6	>100	?
	Zeolite 5A (LTA Zeolite)	3	4.1 x 4.1	1	Ca
	Zeolite 4A (LTA Zeolite)	3	4.1 x 4.1	1	Na
	Sieve S115 (Same as Abscents 3000? Different particle size?)				
25	Zeolite DAY-55	3	7.5?	55	H
	Zeolite M5 (MOR Zeolite)	3 / 1	6.5x 7/2.6x5.7	5	Na
	M. Sieve ETS-4 A titanosilicate	?	<4.0	NA	?
	M.Sieve ETS-10 A titanosilicate	?	8-10	NA	?
30	Zeolite Y52	FAU Zeolite	7.4 x 7.4	2.5	Na
	Zeolite 13X	FAU Zeolite	7.4 x 7.4	1.25	Na

NA NOT APPLICABLE; ? = Not Known.

ZnO/TiO₂ is Zn₂TiO₄-Zn₂Ti₃O₈ from Alfa Inorganics.

35 (1) ZnO/Zn phosphate calcinated mix as prepared in U.S. Patent No. 5,219,542

ZnO/Al salt/Ni salt calcinated mix as prepared in U.S. Patent No. 5,174,919

Magnesium aluminate calcinated as prepared in U.S. Patent No. 5,229,091

Zeolites 4A, 13X and Y52 from Alfa Inorganics.

Zeolite 5A and M5 (Mordenite) from Linde

40 Abscents 3000 and S115 from UOP Corp.

Molecular Sieves ETS-4 and ETS-10 from Englehard Corp.

Chabazite from Minerals Research, mined in Christmas AZ.

All Clays from American Colloid Company.

- Activated Carbon, grade S-5 from Darco.
Zeolite DAY-55 from DEGUSSA. Corp.
VEEGUM A132A is purified smectite clay (hydrated magnesium aluminum silicate) from R.T.Vanderbilt Co. ; VAN GEL B is smectite clay from
- 5 Vanderbilt.Co. They are used in the oil industry to adsorb/react with sulfur compounds.
Zeolite three letter designations are those of the International Zeolite Association.

TABLE 2
ABSORPTION OF H₂S BY POLYMER BLENDS

	<u>SUBSTANCE</u>	<u>%H₂S REMAINING</u>
5	Act. alumina	0
	ZnTi oxide	0
	VEEGUM A132A	0
	VAN GEL B	0
	Mg Aluminate	0
10	ZnO-Al-Ni	29
	ZnO-Zn phosphate	0
	ABSCENTS 3000	23
	Zeolite 5A	0
	Zeolite 4A	0
15	Chabazite	0
	Act. carbon	7
	Zeolite S115	100
	Bentonite (MPS)	100
	Magnebrite HS	0
20	Hectabrite DF	3
	Laponite RD	6

All film samples contained 2 weight percent of the ingredient.

- 25 Films were extruded on a 28MM. co-rotating twin-screw Extruder, having an L/D of 28/1 and 2 mixing sections. A 10 inch film die was used to produce 1 mil film, at a melt temperature of 215-225 deg.C.

TABLE 3
ABSORPTION BY PURE ABSORBANT/REACTANT

	<u>SUBSTANCE</u>	<u>%H₂S REMAINING</u>
	ZnO-Zn phosphate (5.7mg)	9
5	ZnO-Al-Ni (6.4mg)	100
	Zeolite 5A	13
	Zeolite 4A	17
	Zeolite 13X	100
	Abscents 3000	54
10	Zeolite Y52	86
	Zeolite M5	2
	Chabazite	4
	Zeolite DAY-55	0
	M.Sieve S-115	40
15	M.Sieve ETS-4	0
	M.Sieve ETS-10	19
	Magnebrite HS	5
	Bentonite MPS	4
	Bentonite NF	4
20	Hectabrite DF	17
	Laponite RD	6

25 Powder sample weight was 5 mg.

CLAIMS

1. A packaging material for adsorption of sulfur compound odors from foods or non-food protein sources, comprising:
 - a) a particulate aluminosilicate or silica molecular sieve having a three dimensionally-connected pore structure, having pore-openings of minimum diameter 4 Angstroms, a Si/Al atomic ratio of greater than 1, and all of any associated cations those of metals of group 1A or 2A of the Periodic Table, and
 - b) an associated structural supporting component which is an oriented mono- or multilayer polymer film into one or more layers of which the molecular sieve is blended at a concentration of from 0.1 to 10 weight percent.
2. The packaging material of claim 1 wherein food from which the odor is to be adsorbed is fresh, cooked or preserved, and is selected from the group consisting of cheese, meat, poultry, eggs, dairy products and ovalbumin.
3. The packaging material of claim 1, wherein the oriented mono- or multilayer polymer film is a shrink film.
4. The packaging material of claim 1 wherein the associated cations are Na or Ca.
5. The packaging material of claim 4 wherein the minimum diameter of the pore-openings is 5.5 Angstroms.
6. The packaging material of claim 5, wherein the oriented polymer film is a shrink film.
7. A packaging material for adsorption of sulfur compound odors from foods or non-food protein sources, comprising:
 - (a) a particulate aluminosilicate or silica molecular sieve having an adsorption capacity such that 5 mg. placed in a GC vial is capable of adsorbing at least 25% of hydrogen sulfide present in such a vial of volume 22.5 cc., at a concentration of 12,000 ppm in the vial, in 15 minutes at 25 +/- 2 deg.C, and
 - (b) an associated structural supporting component which is an oriented mono- or multilayer polymer film into one or more layers of which the molecular sieve is blended at a concentration of from 0.1 to 10 weight percent.

8. The packaging material of claim 7, wherein the oriented mono- or multilayer polymer film is a shrink film.

5 9. A packaging material for adsorption of sulfur compound odors from foods or non-food protein sources, comprising:

 (a) a particulate aluminosilicate selected from the group comprising, zeolite Y52, zeolite 13X, and

 (b) an associated structural supporting component which is a shrink mono- or
10 multilayer polymer film into one or more layers of which the molecular sieve is blended at a concentration of from 0.1 to 10 weight percent.

 10. The packaging material of claims 1, 8 or 9 in the form of a film package.

15

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/08558

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J20/18 B65D65/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Section Ch, Week 8712 Derwent Publications Ltd., London, GB; Class A17, AN 87-082374 XP002012829 & JP,A,62 032 144 (MITSUI DUPONT POLYC) , 12 February 1987 see abstract	1,10
A	---	4
Y	DATABASE WPI Week 9420 Derwent Publications Ltd., London, GB; AN 94-164063 XP002012830 & JP,A,06 107 847 (FUJI) , 19 April 1994 see abstract ---	1,10
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "&" document member of the same patent family

Date of the actual completion of the international search

9 September 1996

Date of mailing of the international search report

20 -09- 1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Wendling, J-P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/08558

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 9103 Derwent Publications Ltd., London, GB; AN 91-018436 XP002012831 & JP,A,02 290 220 (TOKAI) , 30 November 1990 see abstract ---	1
A	EP,A,0 159 056 (SHELL) 23 October 1985 see page 2, line 16-36 ---	1,4,5
A	EP,A,0 297 543 (UNION CARBIDE CORP.) 4 January 1989 cited in the application ---	
A	DATABASE WPI Week 9402 Derwent Publications Ltd., London, GB; AN 94-011953 XP002012923 & JP,A,05 319 411 (DAINIPPON INK & CHEM) , 3 December 1993 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/08558

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-159056	23-10-85	AU-B- 570101	03-03-88
		AU-B- 4032585	03-10-85
		CA-A- 1230107	08-12-87
		JP-A- 60232234	18-11-85
		US-A- 4673557	16-06-87

EP-A-297543	04-01-89	US-A- 4795482	03-01-89
		AU-B- 602411	11-10-90
		AU-B- 1854288	05-01-89
		AU-B- 614562	05-09-91
		CA-A- 1314275	09-03-93
		DE-A- 3872064	23-07-92
		JP-A- 1085113	30-03-89
		JP-B- 7004503	25-01-95
		KR-B- 9404617	27-05-94
		US-A- 4826497	02-05-89
		US-A- 5254337	19-10-93
		US-A- 4855154	08-08-89
		US-A- 5013335	07-05-91
